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(54) **Ink jet dyeing method for preheated textile.**

(57) In an ink jet dyeing method, a highly absorbing high polymer substance is applied to a cloth of fibers before dyeing the cloth by the ink jet method. The result is that any spread of dye ink on a cloth can be prevented perfectly by applying only a small amount of anti-spread agent to the cloth before dyeing. Because of such a small amount of anti-spread agent, it is possible to retain the texture of cloth and to give an excellent degree of waterproofness even if the anti-spread agent applied to the cloth was not removed by, for example, washing.

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**BACKGROUND OF THE INVENTION****1. Field of the Invention:**

5 This invention relates to an ink jet dyeing method for dyeing various designs clearly and effectively on a surface of a woven, knit or non-woven cloth of various fibers by ink jetting.

**2. Description of the Related Art:**

10 A so-called ink jet dyeing method for dyeing various designs effectively on the surface of a woven, knit or non-woven cloth by ink jetting, which was developed for printing on paper, is disclosed in, for example, Japanese Patent Laid-Open Publication No. Sho 54-18957. Various developments for realizing the ink jet method in the field of dyeing are going on.

For example, attempts have been made to prevent any spread of dye on the surface of a cloth, which is 15 a matter of primary concern in ink jet dyeing on cloth. Generally although it can be expected that the spread of dye on the cloth surface will be reduced if the viscosity of dye ink is increased, the ink tends to stop in the ink jet nozzle so that management of the nozzle would be complicated and smooth operation is difficult to achieve.

Another attempt could be considered to prevent the spread of dye ink by instantaneously vaporizing the 20 solvent upon arrival of the ink at the cloth surface. In this case, however, the cloth must be heated up to a high temperature before dyeing, and as a result, not only the cloth tends to be damaged but also the dye would degenerate which might lead deterioration of products.

Alternatively, a method of preventing the spread of dye ink by applying an anti-spread agent, which adheres to dye and retains it, onto the cloth surface before dyeing is disclosed in, for example, Japanese 25 Patent Publication No. Sho 63-31594. Specifically, at least one kind of compound selected from the group consisting of a water-soluble high polymer, a water-soluble salt and water-soluble inorganic minute particles, which are substantially unable to adhere to dye and are able to retain the dye, is attached to the cloth surface by 1 to 50% in the preparation process, then dye ink is given by ink jetting, whereupon the compound or compounds is heated to fix and is then washed away.

30 The dyeing method disclosed in Japanese Patent Publication No. Sho 63-31594 is effective as it is free of nozzle jamming and deterioration of products. However, though this publication is silent about any mechanism for attaching to the cloth surface the dye retained by the anti-spread agent, there is no denying the fact that the degree of exhaustion would be lowered, compared to that in the case of one and the same dye. Further, since the anti-spread agent, which retains dye, is washed away after the dye is heated to fix, 35 the dye would be removed during washing, which would lower the efficiency of adherence of dye further.

**SUMMARY OF THE INVENTION**

40 it is an object of this invention to provide an ink jet dyeing method which is free of any spread of dye and deterioration of texture of a cloth and high in degree of exhaustion and from which a secondary effect can be expected for the dyed products.

According to this invention, there is provided an ink jet dyeing method for dyeing a cloth of fibers by ink jetting, wherein a highly water-absorbing high polymer is applied to the cloth before ink jetting.

This invention will now be described in detail along with its mode of operation.

45 The ink jet method to be used in this invention should by no means be limited to a particular form. The typical conventional form is exemplified by a electrostatic attraction method in which a typical form, a strong electric field is given between a nozzle and an accelerating electrode forwards of the nozzle and ink particles are jetted from the nozzle according to an information signal, an ultrasonic oscillation method in which ink to be supplied under high pressure is sprayed in minute particles from a nozzle, which is vibrated 50 by a crystal vibrator, according to an information signal, and a piezo component method in which ink is sprayed from a nozzle by giving an electrical signal to a piezo component to apply pressure to ink.

For ink, known dyes such as direct dye, acid dye, chrome dye, reaction dye, dispersion dye or cation dye may be used, depending on the kind of cloth fibers. Dye ink is prepared by adding, to the dye and liquid, various kinds of additives such as an anti-dry agent of, for example, glycol group, a dye solvent, a 55 characteristic adjust agent, an antiseptic, a sterilizer and a chelating agent.

If a design was printed on a fiber cloth with only the above-prepared dye ink by ink jet method, the dye would have spread horribly and so the resulting product would have been a defect. Whereas in this invention, it is possible to retard the spread of dye at least until after the dye is attached to the cloth,

without damaging the texture of the cloth.

An anti-spread agent to be used in this invention is a high polymer compound which is insoluble with water and absorbs much water, i.e. a high polymer substance called "high water-absorbing resin". The high water-absorbing resin is exemplified by vinyl alcohol acrylate, sodium acrylate copolymer, dextrin-acrylate graft copolymer cure and cured polyacrylate salt. Application of the anti-spread agent to the cloth may be performed by a suitable means, such as panting, soaking or spraying.

The individual highly absorbing water-insoluble high polymer compounds has such a characteristic as to instantaneously absorb water tens to thousands times the own weight to gel. Accordingly, if the highly absorbing high polymer compound is applied to the cloth previously, the dye ink will be temporarily absorbed and held by this highly absorbing high polymer compound, and even a definitely small amount of highly absorbing high polymer compound applied will suffice to achieve the original purpose. When the dye is fixed, the water temporarily absorbed by the highly absorbing high polymer compound will be vaporized and the dye held by the same compound will be combined with the fibers to develop a color while the compound also will be attached to the cloth surface to fix.

Since the amount of highly absorbing high polymer compound attached and fixed to the cloth surface is small, the texture of the cloth is kept free from being impaired. As a secondary excellent effect, the compound existing on the cloth surface does not allow raindrops on the front surface to pass to the back surface.

In general, after the development of color, dyeing is finalized by the drying step. Also in the drying step, the highly absorbing high polymer compound fixed on the cloth and serving as an anti-spread agent will not be removed from the cloth, staying in interfiber spaces to give an excellent waterproofness.

## EXAMPLES

This invention will now be described in detail by examples.

### Example 1, Comparative Examples 1 and 2

Three water solutions were prepared each containing tens grams per liter of each of Sumika Gel SP510 (Example 1, colloidal solution; vinyl alcohol acrylate copolymer produced by Sumitomo Chemical Co., Ltd.), Arabia rubber (Comparative Example 1) and montmorillonite (Comparative Example 2). A cloth woven of processed threads made from polyester fibers was soaked in each of the three solutions and was squeezed by 60% using a pad, whereupon the cloth was dried at 100 °C for ten minutes. The resulting cloth was dyed under the following conditions.

#### (1) Preparation of Dispersion Dye Ink:

10% by weight of Dianix Black FG-P (dispersion dye produced by Mitsubishi Chemical-Hechst Co., Ltd.), 15% by weight of polyethylene glycol (average molecular weight: 400), 15% by weight of glycerine and 60% by weight of ion-exchange water were mixed together, and this mixture was pulverized at room temperature by a fine pulverizer such as a sand grinder or a paint conditioner and was filtered by a glass filter 11P5VF (product by Iwaki Glass Co., Ltd., maximum pore diameter: about 1.0  $\mu$ m).

#### (2) Ink Jet Print Conditions:

Type of ink jet method:	on-demand
Nozzle diameter:	60 $\mu$ m
Dot density:	180 dots/inch (vertical, horizontal)
Distance between nozzle and cloth:	1 mm

#### (3) Dyeing Conditions:

The printed cloth was treated to develop color under the following conditions and was then treated by reduction washing, whereupon washing by water, neutralization, washing by water and drying were performed.

Color development:	dry heating at 200 °C for 3 minutes.
Reduction washing:	Soaked at 90 °C for 20 minutes in a bath prepared of hydro-sulfite and sodium hydroxide at proportion of 0.5 grams per liter and 1.0 grams per liter respec-

Neutralization: tively.  
Soaked in an acetic solution (0.1 grams per liter) at 60 °C for ten minutes.

## (4) Results:

Table 1

	Spread	L Value
Example 1	Nil	22.64
Comparative Example 1	Slightly	22.93
Comparative Example 2	Slightly	23.07
Spread: judged by naked eye.		
L Value: a value of brightness of cloth surface by a colorimeter; the darker the color, the smaller the value.		
Colorimeter: COLOR EYE MS-2020 produced by Macbeth Corp.		

Table 1 shows that no spread came out in this invention while spread was found in Comparative Examples, and that the L value in this invention was smaller than those in Comparative Examples.

Example 2, Comparative Examples 3 and 4

Three water solutions were prepared each containing tens grams per liter of each of Sanwet IM-1000MPS (Example 2, dextrin-acrylate salt graft copolymer cure produced by Sanyo Chemical Co., Ltd.), Arabia rubber (Comparative Example 3) and montmorillonite (Comparative Example 4). A cloth woven of processed threads (cloth woven of viscose rayon threads) made from cellulose fibers was soaked in each of the three solutions and was squeezed by 60% using a pad, whereupon the cloth was dried at 100 °C for ten minutes. The resulting cloth was dyed under the following conditions.

## (1) Preparation of Reactive Dye Ink:

10% by weight of C.I. Reactive Black 5 (reactive dye), 15% by weight of polyethylene glycol (average molecular weight: 400), 15% by weight of glycerine and 60% by weight of ion-exchange water were mixed together, and this mixture was stirred at room temperature and was filtered by a glass filter 11P5VF (product by Iwaki Glass Co., Ltd., maximum pore diameter: about 1.0 μm).

## (2) Ink Jet Print Conditions:

Type of ink jet method: on-demand  
Nozzle diameter: 60 μm  
Dot density: 180 dots/inch (vertical, horizontal)  
Distance between nozzle and cloth: 1 mm

## (3) Dyeing Conditions:

The printed cloth was treated to develop color by exposed to saturated vapor at 100 °C for 15 minutes, whereupon washing by water, neutralization by an acetic solution (0.1 grams per liter) and washing by hot water at 90 °C for 10 minutes, and finally washing by water and drying were performed.

(4) Results:

Table 2

	Spread	L Value
Example 2	Nil	34.73
Comparative Example 1	Slightly	35.29
Comparative Example 2	Slightly	34.80

Table 2 also shows that in this invention it is possible to prevent spread of dye ink better than in Comparative Examples.

As is apparent from the foregoing description, according to this invention, it is possible to perfectly prevent any spread of dye ink on a cloth by applying only a small amount of anti-spread agent to the cloth before dyeing. In addition, because of such a small amount of anti-spread agent, it is possible to retain the texture of cloth and to give an excellent degree of waterproofness even if the anti-spread agent applied to the cloth was not removed by, for example, washing.

#### Claims

1. An ink jet dyeing method for dyeing a cloth of fibers by ink jetting, wherein a highly water-absorbing high polymer is applied to the cloth before ink jetting.
2. An ink jet dyeing method according to claim 1, said highly water-absorbing high polymer consists of vinyl alcohol acrylate, sodium acrylate copolymer, dextrin-acrylate graft copolymer cure or cured polyacrylate salt.



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 93 10 7158

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
D,X	DATABASE WPI Week 8618, Derwent Publications Ltd., London, GB; AN 86-115656 & JP-A-61 055 277 (TORAY IND INC) 19 March 1986 * abstract *	1,2	B41M5/00 D06P1/00 D06P1/52
A	--- DATABASE WPI Week 8615, Derwent Publications Ltd., London, GB; AN 86-097108 & JP-A-61 041 586 (CANON KK) 27 February 1986 * abstract *	1,2	
A	--- DATABASE WPI Week 8327, Derwent Publications Ltd., London, GB; AN 83-702592 & JP-A-58 089 391 (FUJI PHOTO FILM KK) 27 May 1983 * abstract *	1,2	
A	--- DATABASE WPI Week 9129, Derwent Publications Ltd., London, GB; AN 91-213281 & JP-A-03 137 283 (TORAY IND INC) 11 June 1991 * abstract *	1,2	B41M D06P
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 JULY 1993	Examiner DELZANT J-F.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

DERWENT-ACC-NO: 1993-353084

DERWENT-WEEK: 199914

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TITLE: Ink jet dye method, on a cloth while  
retaining texture -  
using a highly absorbing polymer  
substance to pretreat  
textile before dyeing

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PATENT-ASSIGNEE: YOSHIDA KOGYO KK[YOSI] , YKK CORP[YOSI],  
YKK KK[YOSI]

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PATENT-FAMILY:

PUB-NO	PAGES	PUB-DATE	
LANGUAGE		MAIN-IPC	
EP 568955 A1		November 10, 1993	E
006	B41M	005/00	
KR 9604639 B1		April 11, 1996	N/A
000	D06P	001/00	
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CN 1080972 A		January 19, 1994	N/A
000	D06P	005/00	

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CITED-DOCUMENTS: JP 03137283; JP 58089391 ; JP 61041586 ;  
JP 61055277

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APPL-DATE		
EP 568955A1	N/A	

1993EP-0107158	May 3, 1993
KR 9604639B1	N/A
1993KR-0007836	May 7, 1993
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1993CA-2094100	April 15, 1993
CN 1080972A	N/A
1993CN-0105460	May 3, 1993

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D06P001/58 ,  
D06P005/00

ABSTRACTED-PUB-NO: EP 568955A

#### BASIC-ABSTRACT:

An ink jet dyeing method for dyeing a cloth of fibres by ink jetting involves a highly water-absorbing high polymer being applied to the cloth before ink jetting.

The highly water-absorbing high polymer may pref. be vinyl alcohol acrylate, sodium acrylate copolymer, dextrin-acrylate graft copolymer cure or cured polyacrylate salt.

In an example, 2 water solns. were prepd., each contg. 10g/l of Sumika Gel SP510 (RTM-colloidal soln. vinyl alcohol acrylate copolymer and Arabia rubber). A cloth woven of processed threads made from polyester fibre was soaked in each of the solns. and was squeezed by 60% using a pad. The cloth was dried at 100 deg. C for 10 mins. and was then dyed. It was found that no spread came out of the sample prepd. with the vinyl alcohol acrylate whereas slight spread was noted in the other sample. The cloth prepd. with the acrylate was also brighter than the other sample. USE/ADVANTAGE - Any spread



of dye ink on a  
cloth can be prevented perfectly by applying only a small  
amt. of an antispread  
agent to the cloth before dyeing. It is possible to retain  
the texture of  
cloth and give an excellent degree of waterproofness, even  
if the anti-spread  
agent applied was not removed.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: INK JET DYE METHOD CLOTH RETAIN TEXTURE HIGH  
ABSORB POLYMER  
SUBSTANCE PRETREATMENT TEXTILE DYE

ADDL-INDEXING-TERMS:  
VINYL! ALCOHOL ACRYLATE!

DERWENT-CLASS: A87 F06 P75

CPI-CODES: A12-G; F03-C06; F03-F31;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

017 ; G0339\*R G0260 G0022 D01 D12 D10 D51 D53 D63 F41 ;  
A999 A215  
; A999 A782 ; P1730 P1694 ; H0011\*R ; S9999 S1616 S1605  
; P0088

Polymer Index [1.2]

017 ; R24001 G0282 G0271 G0260 G0022 D01 D12 D10 D51  
D53 D58 D61  
D83 F36 F35 Na 1A ; A999 A215 ; A999 A782 ; H0011\*R ;  
S9999 S1616  
S1605 ; P0088

Polymer Index [1.3]

017 ; G0282\*R G0271 G0260 G0022 D01 D12 D10 D51 D53 D58  
D83 F36  
F35 D61\*R H0146 ; R03275 R01863 D01 D11 D10 D23 D22 D31  
D42 D50  
D86 F24 F29 F26 F34 H0293 M2313 P0599 G3623 ; A999 A215  
; A999 A782  
; H0011\*R ; H0088 H0011 ; M9999 M2073 ; S9999 S1616  
S1605 ; P0088

Polymer Index [1.4]

017 ; G0282\*R G0271 G0260 G0022 D01 D12 D10 D51 D53 D58  
D83 F36  
F35 D61\*R ; A999 A215 ; A999 A782 ; H0000 ; M9999 M2073  
; S9999

S1616 S1605 ; P0088  
Polymer Index [1.5]  
017 ; B9999 B3407 B3383 B3372  
Polymer Index [2.1]  
017 ; P0839\*R F41 ; S9999 S1194 S1161 S1070  
Polymer Index [2.2]  
017 ; ND00 ; N9999 N5798 N5787 N5765 ; B9999 B5356  
B5276 ; B9999  
B3509 B3485 B3372 ; ND07 ; K9927

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials: 0003 0039 0041 0042 0044 0045 0047 0048 0050  
0051 0053 0222 0228  
0229 0409 0410 0487 1288 1989 2006 2007 2008 2020 2308 2324  
2509 2660 2821 3250  
3251  
Multipunch Codes: 017 034 037 06- 074 075 076 081 09& 09-  
10& 10- 15- 17& 230  
231 244 245 259 303 311 398 473 52& 532 533 535 57- 601 688  
722 017 03& 03- 143  
364 366 367 53& 532 533 535 597 600 601 664 667

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